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TITLE: LUMINESCENCE FROM DEFECTS AND IMPURITY CENTERS IN YTTRIUM OXIDE

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LUMINESCENCE FROM DEFECTS AND IMPURITY CENTERS IN Y_2O_3

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ABSTRACT

High-purity (99.999%) Y_2O_3 powder is used as a starting material for fabricating high-temperature superconductors (HTS), and is frequently found as an unreacted second phase in the final product. We have found that as-received Y_2O_3 contains Tb^{3+} paramagnetic impurity ions as determined by TSL and emission-spectra measurements. Deep luminescence traps (presumably Tb^{4+} ions) are formed in Y_2O_3 when it is exposed to γ-rays, x rays, or fluorescent lights. These deep traps can only be removed by annealing the material to near 1600°C. Given the short coherence length of HTS it is possible that order-of-magnitude variations in the Tb impurity concentration of starting materials may affect the ultimate value of surface resistance (R_s).

INTRODUCTION

Yttrium oxide Y_2O_3 is a trivalent metal oxide which has a cubic structure with space group T_h^7. The unit cell contains 32 cations and 48 anions; each anion is surrounded by four cations in a distorted tetrahedron. It has a large number of inequivalent sites for defects and substitutional impurities and, therefore, accepts rare-earth ions in the trivalent state without charge-compensating problems and ion-size limitations. For example, when activated with rare-earth ions yttrium oxide exhibits selective photoluminescence in the visible and near ultraviolet spectral region[1] and represents an interesting host material for many phosphors.

In yttrium-based HTS, Y_2O_3 is used as one of the starting compounds and is frequently found in sintered $YBa_2Cu_3O_x$ as an unwanted second phase. Removal of this insulating impurity, especially at the surface, is important for acheiving low values of surface resistance, which is important for practical applications of HTS. A convenient method for detecting the presence of insulating materials in HTS, especially at the surface, is that of thermally stimulated luminescence (TSL).[2] Following γ, x, or ultraviolet irradiation at room temperature and subsequent heating to 350°C, Y_2O_3 emits characteristic luminescence, which can be used to identify its presence in HTS. Our objective is to investigate impurities in pure (99.999%) Y_2O_3 by luminescence methods and to utilize this information in fabricating improved HTS materials.

MATERIALS AND METHODS

High-purity (99.999%) powders of Y_2O_3 were obtained from Research Chemicals , Aldrich, and Johnson Matthey, Inc., and were used without further purification. Pressed pellets of these powders were prepared and identified as sample A (Research Chemicals), sample B (Aldrich), and sample C (Johnson Matthey, Inc.). Another group of samples was prepared by intentionally doping virgin Johnson Matthey Y_2O_3 powder with Tb. The resulting concentrations, as determined by chemical analyses, were 1, 2, 11, and 150 ppm by weight.

Gamma irradiation was provided by a ^{60}Co source whose exposure rate at sample site was 5.1×10^4 R/hr. X-irradiation was provided by a machine operating at 55 kV and 40 mA yielding an exposure rate of 9×10^5 R/hr at the sample. TSL glow curves (total light output as a function of temperature) were recorded by a commercial TLD reader. For the reasons discussed below, all samples were annealed at 1600°C and stored in a dark environment prior to each TSL measurement.

RESULTS AND DISCUSSION

All Y_2O_3 samples used in this study produce TSL when exposed to γ-rays, x rays, or fluorescent light at room temperature and are subsequently heated to 350°C. The typical glow curve exhibits luminescence peaks at 115 and 190°C, with the exact peak value being determined by the Tb content. More interesting than the glow curve is its spectral content because it provides a distinct signature of the Tb impurity. Shown in Fig. 1 are the emission spectra observed from the as-received samples of Y_2O_3 along with the emission spectrum of an intentionally doped (150 ppm-Tb) sample. Each spectrum consists of a broad band with a maximum near 360 nm (3.4 eV) and several groups of narrow bands in the regions near 480, 550, 575, 620, and 670 nm. The broad band-emission at 3.4 eV is intrinsic to all Y_2O_3 materials which have a band edge at ~ 6.5 eV, and is associated with barrierless self-trapped excitons.[3] Trapping of excitons (a pair consisting of an electron and positive hole in the forbidden band) is known to be associated with lattice defects. The narrow bands on the other hand are the well-known $^5D \rightarrow {}^7F$ transitions of the Tb^{3+} ion: $^5D_4 \rightarrow {}^7F_6 \Rightarrow$ 480 nm, $^5D_4 \rightarrow {}^7F_5 \Rightarrow$ 550 nm, $^5D_4 \rightarrow {}^7F_4 \Rightarrow$ 575 nm, $^5D_4 \rightarrow {}^7F_3 \Rightarrow$ 620 nm, and $^5D_4 \rightarrow {}^7F_2 \Rightarrow$ 670 nm.[1,4,5] These spectral lines are observed in samples A, B, and C, although the intensity associated with the latter two samples is significantly reduced from that of sample A. To confirm that Tb is indeed the impurity which produces the line spectrum found in Y_2O_3, we intentionally doped sample C and recorded its spectrum. As shown in the lower panel of Fig. 1, this spectrum is identical to that of sample A.

To further demonstrate the effect of Tb impurities on the TSL of Y_2O_3, we recorded the integrated TSL output (in μC/gm) as a function of known Tb concentration. The results are shown in Fig. 2. A comparison of these results with the

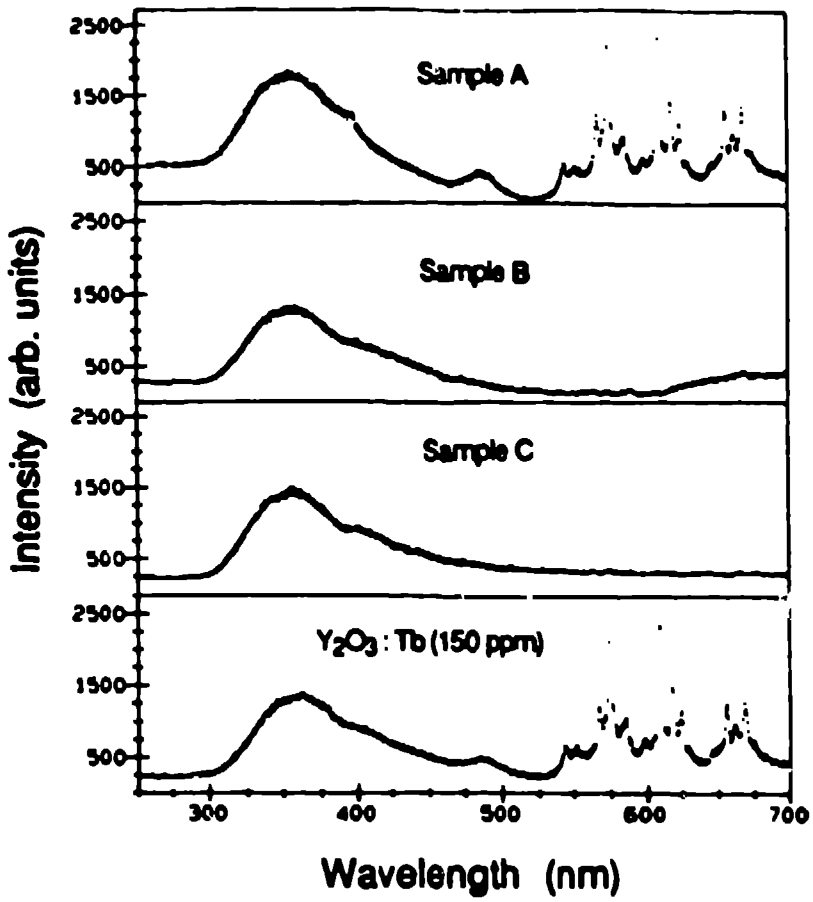

Fig. 1. Emission spectra of samples A, B and C, and of intentionally Tb-doped Y_2O_3.

TSL outputs of samples A, B, and C, which have unknown Tb concentrations, provides estimates of the unknown Tb concentrations. Note that here we are measuring the area under the TSL glow curve and not the area under the spectral peaks. Accordingly, we conclude that samples A, B, and C contain approximately 15, 2, and 2 ppm Tb by weight, respectively.

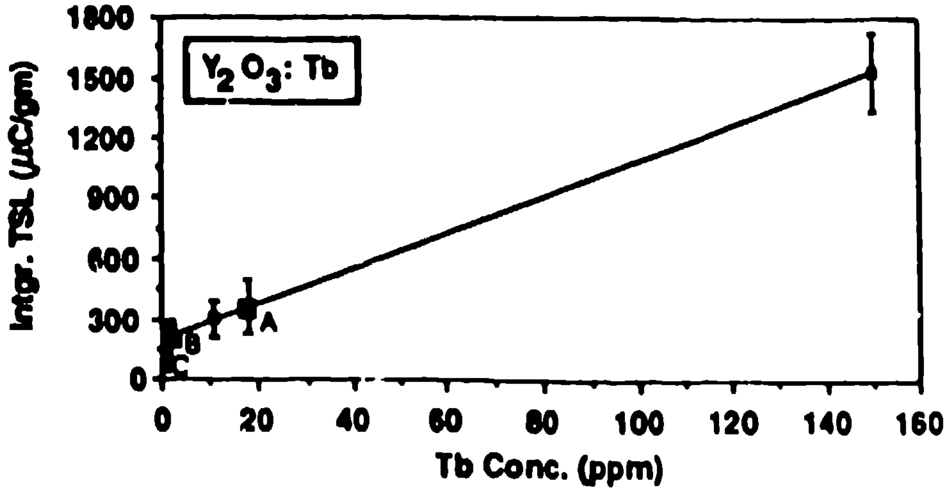

Fig. 2. Integrated TSL vs. Tb concentration. Open squares denote samples with known Tb concentrations and closed squares denote samples A, B, and C

Y_2O_3 was found to be very sensitive to room lights as observed from the TSL of unirradiated, as-received powders. That is, exposure to ordinary fluorescent lights induced a TSL signal. It was verified that preservation of this material in a dark enclosure prevented it from trapping light-induced charges.

Another striking luminescence property of Y_2O_3 is that it yields a large residual TSL signal. In general, radiation-induced electron traps, which produce TSL, are emptied by heating the sample to near 400°C. Assuming that a sample had not received any additional radiation exposure, a subsequent heating cycle should not produce TSL. Contrary to this expectation, we found that subsequent heating cycles of Y_2O_3 produced significant luminescence. The TSL intensity decreased and the glow peaks (maxima in the luminescence vs. temperature curves) occurred at progressively higher temperatures in each subsequent measurement. This phenomenon is attributed to the formation of Tb^{4+} ions, which act as deep traps.[6] By following careful annealing techniques it was determined that the deep traps could be emptied and the sample could be returned to its pristine state by annealing to near 1600°C. Note that for this reason, and that mentioned above, all TSL measurements were done on samples which were previously annealed at 1600°C and stored in a dark environment.

In summary, we have demonstrated that Y_2O_3 (99.999%), which is commonly used as the starting material for synthesizing HTS materials, contains Tb^{3+} paramagnetic impurity ions. This study also reveals that Y_2O_3 is very sensitive to room light and forms deep traps (Tb^{4+} ions), which cannot be removed without annealing near 1600°C. From a practical standpoint, we find that although the Tb impurity concentrations are low in all samples investigated, there are measurable differences in the values of R_s of HTS materials prepared from the different starting materials. Given the short coherence length of HTS in general, it is possible that order-of-magnitude variations in the Tb impurity concentration may affect the ultimate value of R_s. Systematic investigations are underway to examine this intriguing possibility.

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